Atmos. Chem. Phys. Discuss., 9, C6017–C6023, 2009
www.atmos-chem-phys-discuss.net/9/C6017/2009/

Atmospheric
Chemistry
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Discussions

Interactive comment on "Evaluation of the volatility basis-set approach for the simulation of organic aerosol formation in the Mexico City metropolitan area" *by* A. P. Tsimpidi et al.

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Received and published: 19 October 2009

This work is aimed at incorporating several relatively new developments in the chemistry of organic aerosol into an existing model, with application to the Mexico City Metropolitan Area. This is an important study, as it shows that such changes bring modeled aerosol loadings (both primary and secondary) more in line with measurements than models typically do. At the same time, the authors are careful not to overinterpret the results. This paper is certainly worthy of publication in ACP. Prior to publication I recommend a few substantial changes, listed below. Most involve expanding the explanation of the model or the discussion of the results, which are glossed over in several places.

1. *P. 13699, line 27 (and elsewhere): I find the term "non-traditional SOA" to be confusing and not terribly helpful. The SOA itself is completely "traditional"; it conforms perfectly to the earliest definition of SOA that I can find (which is by one of the authors of this paper!): particles "formed in the atmosphere by the condensation of low vapor pressure products of the oxidation of organic gases" (Pandis et al., 1992). But the term also apparently doesn't mean "SOA formed from precursors not traditionally included in models", because the authors consider SOA from isoprene (which wasn't regularly included in models until 2006-2007) to be "traditional". Instead "non-traditional SOA" apparently means "SOA from precursors of volatilities not traditionally considered in models, not counting those originally emitted as primary OA." Why not simply classify the SOA by the volatility of the precursor? This gives "V-SOA" (SOA from VOCs), "ISOA" (SOA from IVOCs), and "S-SOA" (SOA from semivolatiles). These aren't ideal labels, but they are less confusing and arbitrary than "Traditional SOA", "Non-Traditional SOA", and "OPOA".*

This is a good suggestion. In the revised manuscript the terminology for the major OA components has been changed following this recommendation by the reviewer.

2. *Section 2.1: It is unclear to what extent the different aerosol types are lumped within the volatility bins. One of the oft-cited benefits of the volatility basis set is that it enables lumping among different aerosol types, keeping the number of tracked species relatively manageable. Were bins from different SOA precursors lumped? (If so, what was done about the differing molecular weights?) Were they lumped with POA?*

The volatility basis set does allow a wide selection of lumping schemes ranging from the "engineering version" where all the OA species are lumped into 4 or so volatility bins to very detailed schemes where the organics related to each source or precursor are simulated separately. The choice does depend on the application. Here we have selected an intermediate level of detail simulating separately POA, OPOA, anthropogenic

SOA from different precursors and biogenic SOA. There was some lumping of SOA from different precursors (e.g., monoterpenes) and the corresponding average molecular weight was used. There was no lumping of POA with SOA. The 9 SOA categories are shown in Table 1.

3. *P. 13706: More details are required about how the background OA is treated. I assume it is treated as nonvolatile and unreactive? If so, it would seem to be somewhat problematic to include biomass burning OA in with this, given that it's semivolatile and subject to further atmospheric oxidation (Grieshop et al., 2008).*

We assume that the background OA has already aged enough in the atmosphere and at the time that it enters the domain through the boundaries it has very low volatility and remaining reactivity. This important point has been clarified in the revised manuscript.

4. *Section 4: a major difference between this model treatment and previous ones is that "aging" of the organics is included. Therefore the effect of this aging needs to be discussed. How much additional oxidation (in terms of average number of reactions with OH) do the SOA and POA components undergo? This is important not just for understanding the role of aging, but also for model-measurement comparisons. For example, if the OPOA is formed from only one OH+SVOC reaction, the O/C ratio of the resulting aerosol is probably not high enough to be considered "OOA" (Presto et al., 2009).*

Unfortunately, in the present modeling framework it is not possible to explicitly calculate the number of reactions with OH that the SOA and POA components undergo. A rough calculation can be made by using the aging rate constant and the corresponding OH levels in the simulation resulting in one generation of oxidation every few hours. This allows the POA to undergo a few generations of oxidation inside the modeling domain. During this period of course the corresponding SOA and POA components are advected out of Mexico City, are mixing with cleaner air from the areas outside Mexico

City. We can, however, quantify the OA mass contributed by these aging reactions. The OPOA is explicitly shown in Figures 5, 6 and 10 of the original paper and its contribution is modest. The aging of the anthropogenic SOA roughly doubles its concentration in CENICA. Information about the amount of the extra oxygenated organic mass resulting from the implementation of the aging reactions has been added to the manuscript.

5. *P. 13707, lines 24-28: why exactly is calculated ("traditional") SOA so much higher in this case? Is this from the NOx dependence? The aging of the aerosol? The use of four model semivolatiles (volatility basis set) rather than just two (Odum model)? Or is it simply from the new aromatic yield parameters from recent chamber studies?*

There are different effects on the SOA concentration from each of these model modifications. The NOx dependence actually decreases the predicted SOA concentration, while both the updated aromatic yields and the aging along with the volatility basis set cause a significant increase. The increased traditional SOA is mainly due to the higher aromatic yields and the subsequent chemical aging. The contributions of each of these modifications to the predicted SOA are now discussed in Section 4.

6. *Section 6: In this section (as well as in the previous paragraph) the uncertainties in the modeled OA, and caveats with comparing model and AMS data, are laid out very nicely. However, the discussion in this section is focused entirely on model inputs, and there is little consideration of uncertainties in the model itself. A particularly large unknown is how organic aerosol changes upon further oxidation ("aging"). Here it is assumed that each oxidation step lowers the vapor pressure by a factor of 10 (and increases mass slightly). This is about the same as saying each oxidation step involves addition of one carbonyl group to the carbon skeleton. That is a reasonable first guess, but given that we know that gas-phase oxidation can lead to larger decreases in volatility (addition of multiple/different functional groups) or even increases in volatility (by fragmentation reactions), such an assumption introduces a large amount of uncertainty to any treatment of aging. (The relationship between aging product distribution* *and NOx – which may be different from the NOx-dependence of SOA from small organics – increases this uncertainty further.) Simulations aimed at understanding how the choice of aging parameters affect predicted OA loading would be extremely useful here (and would increase the impact of this study).*

The sensitivity of the volatility basis set to the aging scheme has been explored in previous work by our group (Shrivastava et al., 2008; Lane et al., 2008a). Please note that the product of the rate constant and the change in volatility is the relevant parameter (it corresponds roughly to the rate of decrease of the volatility) that has been constrained by the few available laboratory measurements. We have chosen therefore to focus here our analysis on the sensitivity of our results to the volatility distribution of the emissions, something that had not been sufficiently investigated by previous studies. We do agree with the reviewer that additional sensitivity analysis is always welcome in such modeling applications. We plan to conduct these in future work for Mexico City focusing on the MILAGRO campaign for which there are enough data to evaluate the effect of the aging scheme assumptions on the spatial distribution of the OA concentrations and to constrain this with the measurements that are available in the T1 and T2 sites. Please note that a similar point has been made by the first reviewer (first comment).

Other points:

7. *Section 2.1: a simple schematic figure illustrating the different aerosol types and chemical processes modeled may be helpful for laying out the general modeling scheme (and the unique aspects of the present work).*

A new figure, illustrating the organic aerosol scheme, has been added to the revised manuscript.

8. *P. 13696, lines 14-15: this (important) sentence seems out of place, given this is a general introduction to the topic.*

This sentence has been moved to Section 3.

9. *P 13702, lines 2-4: the possibility of a complex NOx dependence is alluded to here, but is never followed up on in sections 4-5. To what degree was SOA formed under low-NOx conditions?*

SOA was formed under high-NOx conditions in the urban center and under low-NOÂňx conditions in the surrounding areas. This prediction by the model is consistent with the available measurements in Mexico City. Discussion of this point has been added in Section 4.

10. *P. 13704 (and throughout): IVOCs are repeatedly referred to as “missing”, which is an unusual term. “Unmeasured” is probably a better descriptor.*

We have made the suggested change.

11. *P. 13704, lines 18-21: I’m unclear as to what this means. Do derived vapor pressures agree to within a factor of 10? If so, what are the exact values of c*?*

We have rephrased this sentence to avoid confusion. We now state that these thermodenuder measurements have provided evidence that the Mexico City POA is semivolatile.

12. *Table 2: the second line (starting with “VOC”) should also be part of the header of the table rather than part of the table body.*

This has been corrected.

13. *Table 3: differing volatilities of IVOCs are likely caused by differences in molecular weight; however in this work all are assumed to the same molecular weight (roughly* *that of a C18 alkane, which is relatively volatile). Differences in molecular weight would change the oxidation rates (which are dependent on moles rather than mass); does this affect results?*

The choice of an average molecular weight for all IVOCs does not affect the results. This choice was necessitated by the lack of information about these compounds and our effort to avoid making too many arbitrary parameter choices. For the same reason the same aging rate constant has been used for all species, even if it should depend on the size of the molecule.

14. *Figure 5 (and accompanying discussion, p. 13707): it should be made clear that these fractions do not include background OA.*

The background OA is in fact included in these fractions and is assumed to be a mixture of aged primary and secondary organic aerosols. This is now clarified in the paper to avoid misunderstandings.

15. *Figures 5-6: the color scales differ in each panel; they should be the same for easy comparison.*

The color scales have been changed.

Interactive comment on Atmos. Chem. Phys. Discuss., 9, 13693, 2009.